(12) UK Patent Application (19) GB (11) 2 059 432 A

(21) Application No 8030540
(22) Date of filing 22 Sep 1980
(30) Priority data
(31) 2938868
(32) 26 Sep 1979
(33) Fed. Rep. of Germany (DE)
(43) Application published 23 Apr 1981
(51) INT CL[3] C09K 3/18
(52) Domestic classification C4X 1
(56) Documents cited None
(58) Field of search C4X
(71) Applicants
The British Petroleum Company Limited, Britannic House, Moor Lane, London EC2Y 9BU
(72) Inventors
Wolfgang Ernhardt, Werner Rommel, Wolfram Rudolf Walter Sokolowski, Dieter Rudolf Gustav Wagnitz
(74) Agent
H. L. Eastman, BP Trading Limited, Patents and Licensing Division, Chertsey Road, Sunbury-

(54) Anti-freeze composition

(57) Anti-freeze for coolant liquids, is characterised by the following composition:

a) 1.0 to 4.0 per cent by weight of an alkali salt of boric acid,
b) 0.03 to 0.3 per cent by weight of alkali silicate,
c) 0.05 to 1.0 per cent by weight of alkali hydroxide,
d) 0.03 to 0.2 per cent by weight of benztriazole,
e) 0.03 to 0.3 per cent by weight of nitrophenols or their alkali salts, possibly substituted with methyl radicals,
f) 0.05 to 0.3 per cent by weight of alkali nitrite
g) 0.05 to 0.4 per cent by weight of alkali nitrate,
h) 0.01 to 0.3 per cent by weight of alkanolamine,
i) 0.005 to 0.3 per cent by weight of ethoxylated mercaptobenzimidazole,
k) remainder: 1,2-alkyleneglycols and possibly small quantities of water as solubiliser.

The alkali hydroxide is present in a quantity such that when the anti-freeze compound is diluted with water in the proportion of 1:1 to 1:3 there results a pH of 8.0 to 9.0.

ERRATA

SPECIFICATION No. 2 059 432 A

Page 1, line 42, *for* nitrates (first occurrence) *read* nitrites
Page 8, line 24, *for* nitrate *read* nitrite
THE PATENT OFFICE
21st May, 1982

GB 2 059 432 A

SEE ERRATA SLIP ATTACHED

(12) UK Patent Application (19) GB (11) 2 059 432 A

(21) Application No 8030540
(22) Date of filing 22 Sep 1980
(30) Priority data
(31) 2938868
(32) 26 Sep 1979
(33) Fed. Rep. of Germany (DE)
(43) Application published 23 Apr 1981
(51) INT CL[3] C09K 3/18
(52) Domestic classification C4X 1
(56) Documents cited None
(58) Field of search C4X
(71) Applicants
The British Petroleum Company Limited, Britannic House, Moor Lane, London EC2Y 9BU
(72) Inventors
Wolfgang Emhardt, Werner Rommel, Wolfram Rudolf Walter Sokolowski, Dieter Rudolf Gustav Wagnitz
(74) Agent
H. L. Eastman, BP Trading Limited, Patents and Licensing Division, Chertsey Road, Sunbury-on-Thames, Middlesex TW16 7LN

(54) Anti-freeze composition

(57) Anti-freeze for coolant liquids, is characterised by the following composition:

a) 1.0 to 4.0 per cent by weight of an alkali salt of boric acid,

b) 0.03 to 0.3 per cent by weight of alkali silicate,

c) 0.05 to 1.0 per cent by weight of alkali hydroxide,

d) 0.03 to 0.2 per cent by weight of benztriazole,

e) 0.03 to 0.3 per cent by weight of nitrophenols or their alkali salts, possibly substituted with methyl radicals,

f) 0.05 to 0.3 per cent by weight of alkali nitrite

g) 0.05 to 0.4 per cent by weight of alkali nitrate,

h) 0.01 to 0.3 per cent by weight of alkanolamine,

i) 0.005 to 0.3 per cent by weight of ethoxylated mercaptobenzimidazole,

k) remainder: 1,2-alkyleneglycols and possibly small quantities of water as solubiliser.

The alkali hydroxide is present in a quantity such that when the anti-freeze compound is diluted with water in the proportion of 1:1 to 1:3 there results a pH of 8.0 to 9.0.

GB 2 059 432 A

SEE ERRATA SLIP ATTACHED

SPECIFICATION

Anti-freeze

The present invention relates to an anti-freeze suitable for use in the cooling system of an automobile.

The progressive development in automobile construction is leading to designs which require particularly little maintenance. Thus, in the case of many car engines it is expected that the cooling liquids will remain in the system for at least 2 years.

Parallel with this development, more and more light metal alloys are being used in engine construction with a view to economising on weight and costs. Furthermore design measures which are necessary from the environmental protection and energy conservation points of view are leading to an ever greater thermal load on the coolant liquids.

The metals or metal alloys used in the cooling system are all at risk from corrosion, but the light metals, because of their position in the electrochemical series of elements are particularly prone to chemical attack. There is the additional effect that the metallic parts are connected to each other and together with the coolant liquid form galvanic cells.

In order to prevent corrosion in coolant systems, numerous corrosion inhibitors have been proposed and used in anti-freeze formulations. The best known are borax, alkali nitrites, salts of benzoic acid, salts of phosphoric acid, alkali carbonates, alkali hydroxides, amines, alkanolamines, benztriazole, sodium mercaptobenzthiazole and sodium metasilicate. The individual inhibitors generally only produce their corrosion-reducing effect for a single metal or a small group of metals. Hence, for a satisfactory anti-freeze compound, various inhibitors have to be combined with each other. However, many of the known additives possess negative as well as positive properties in respect of their corrosion inhibiting behaviour. They may have a corrosion-reducing effect on some metals while at the same time, promoting the attack by the coolant liquid on other metals. By combining inhibitors, one may even suppress the favourable properties whilst the unfavourable properties are reinforced. Therefore in formulating an anti-freeze a careful selection of compatible additives must be made. When making this choice the effect of the anti-freeze compound must be determined in tests which closely approximate to practical conditions because predicting the properties of an anti-freeze formulation on the basis of the properties of the individual components is generally impossible or only possible to a very limited extent.

An anti-freeze which satisfies most of these requirements is described in German Patent DE PS 14 92 522. However, certain problems have been identified in the use of these formulations. The first problem is a decrease of the anti-corrosion properties when the concentration of the anti-freeze in the coolant liquid is low. In the event of loss of coolant, the cooling system is often topped up with water, especially in summer. As a result, the concentration of the anti-freeze compound is reduced and may become so low that the corrosion protection effect originally present in the coolant is substantially reduced or lost completely. The second difficulty is that the corrosion protection afforded to special aluminium alloys by the known anti-freeze compounds is not particularly good.

The applicants have discovered an anti-freeze formulation which overcomes these problems.

Thus, according to the invention, an anti-freeze, suitable for use in the cooling system of an automobile, which anti-freeze contains 1,2 alkylene glycols, alkali salts of boric acid alkali silicates, benztriazole, ethoxylated mercaptobenzimidazole, nitrophenols or their alkali salts which may be substituted with alkyl radicals, alkali nitrates, alkali nitrates alkanolamines and alkali hydroxides, the alkali hydroxides being present in a quantity such that when the anti-freeze is diluted with water in a ratio of 1:1 to 1:3 there results a pH of 8.0 to 9.0, is characterised by the following composition:

a) 1.0 to 4.0 per cent by weight of an alkali salt of boric acid,
b) 0.03 to 0.3 per cent by weight of alkali silicate,
c) 0.05 to 1.0 per cent by weight of alkali hydroxide,
d) 0.03 to 0.2 per cent by weight of benztriazole,
e) 0.03 to 0.3 per cent by weight of nitrophenols or their alkali salts, possibly substituted with methyl radicals,
f) 0.05 to 0.3 per cent by weight of alkali nitrite,
g) 0.05 to 0.4 per cent by weight of alkali nitrate,
h) 0.01 to 0.3 per cent by weight of alkanolamine,
i) 0.005 to 0.3 per cent by weight of ethoxylated mercaptobenzimidazole,
k) remainder: 1,2-alkyleneglycols and possibly small quantities of water as solubiliser.

Particularly preferred anti-freeze compounds of the Invention possess the following composition:

a) 2.5 to 3.5 per cent by weight borax or
b) 1.3 to 1.8 per cent by weight disodium tetraborate,
c) 0.05 to 0.1 per cent by weight benztriazole,
d) 0.05 to 0.15 per cent by weight picric acid,
e) 0.10 to 0.20 per cent by weight sodium nitrite,

f) 0.20 to 0.30 per cent by weight potassium nitrate,
g) 0.05 to 0.15 per cent by weight sodium metasilicate-pentahydrate,
h) 0.05 to 0.15 per cent by weight triethanolamine,
i) 0.01 to 0.2 per cent by weight ethoxylated mercaptobenzimidazole,
k) 0.1 to 0.5 per cent by weight sodium hydroxide,
l) remainder: ethyleneglycol and/or 1,2-propyleneglycol and also possibly small quantities of water as solubiliser.

Particularly good protection for iron and non-ferrous metals may be obtained by adding 0.005 to 0.3 per cent by weight, preferably 0.01 to 0.2 per cent by weight of mercaptobenzthiazole, preferably sodium mercaptobenzthiazole, to the anti-freeze compounds of the invention.

If the anti-freeze compounds of the invention are used in high concentrations, an addition of sodium hexafluorosilicate and/or lead nitrate in quantities of 0.001 to 0.3, preferably 0.01 to 0.05 per cent by weight may be advantageous.

The anti-freeze compounds of the invention may also contain anti-foam agents, for example silicone fluid, polyether or tributylphosphate.

It is true that cavitation in cooling systems is best prevented by design measures, but to a certain extent there exists the possibility of reducing cavitation by additions to the anti-freeze formulation. In this connection, for the anti-freeze compounds of the invention, the sodium salt of a copolymer of maleic anhydride and methylvinylether and also monophosphoric or diphosphoric ester of tributylphenyltetraglycol ether have proved to be suitable.

Wherever alkali compounds have been mentioned above, sodium or potassium compounds are the ones which are preferred.

Preferred alkali salts of boric acid are borax, disodium tetraborate or sodium metaborate.

The preferred nitrophenol is picric acid. However, other water-soluble and glycol-soluble alkylnitrophenol compounds may also be used, in which case it is mainly methyl which is concerned as the alkyl substituent. Examples of this are phenol compounds with up to three nitro groups and up to three methyl groups, especially o-nitrophenols, m-nitrophenols, p-nitrophenols, 2,4-di-nitrophenols, 2,6-di-nitrophenols, 2,4,6-trinitrophenols, nitrocresols, dinitrocresols, trinitrocresols, mononitroxyenols, dinitroxylenols and trinitroxylenols.

Preferred alkanolamines are trialkanolamines such as triethanolamine and tripropanolamine. Alkoxy alkanolamines may also be used.

The alkali hydroxide is preferably added in the form of a 50% solution in water to the anti-freeze compound. The water used for this may at the same time act as a solubiliser for this and other components. A minimum of water is used to get the best results.

The ethoxylated mercaptobenzimidazole is preferably a reaction product from mercaptobenzimidazole and ethylene oxide, which has 5 to 10 ethylene oxide groups per molecule. The average number of ethoxy units per molecule amounts, in a typical product which was also used in the Examples, to about 8. This ethoxylated mercaptobenzimidazole also has the following physical properties:

Solidification point	below —17°C
Boiling point	205°C
Viscosity at 20°C	1946 cSt
Density at 20°C	1.19 g/cm^3

Preferred 1,2-alkyleneglycols are ethylene and propyleneglycol.

The following Examples illustrate the invention. The following mixtures were produced:

EXAMPLE 1

Borax	3.00 per cent by weight
1,2,3-benztriazole	0.05 per cent by weight
Picric acid	0.09 per cent by weight
Sodium nitrite	0.10 per cent by weight
Potassium nitrate	0.25 per cent by weight

EXAMPLE 1 — Continued

Sodium metasilicate-pentahydrate	0.10 per cent by weight
Triethanolamine	0.10 per cent by weight
Caustic soda solution (50%)	0.80 per cent by weight
Ethoxylated mercapto-benzimidazole	0.10 per cent by weight
Water	0.50 per cent by weight
Ethyleneglycol	94.91 per cent by weight

EXAMPLE 2

Disodiumtetraborate	1.59 per cent by weight
Picric acid	0.09 per cent by weight
1,2,3-benztriazole	0.05 per cent by weight
Sodium nitrite	0.10 per cent by weight
Potassium nitrate	0.25 per cent by weight
Sodium metasilicate-pentahydrate	0.10 per cent by weight
Caustic soda solution (50%)	0.60 per cent by weight
Triethanolamine	0.10 per cent by weight
Ethoxylated mercapto-benzimidazole	0.10 per cent by weight
Ethyleneglycol	97.02 per cent by weight

EXAMPLE 3

Disodiumtetraborate	1.59 per cent by weight
Picric acid	0.09 per cent by weight
1,2,3-benztriazole	0.05 per cent by weight
Sodium nitrite	0.10 per cent by weight
Potassium nitrate	0.25 per cent by weight
Sodium metasilicate-pentahydrate	0.10 per cent by weight
Triethanolamine	0.10 per cent by weight
Caustic soda solution (50%)	0.60 per cent by weight
Ethoxylated mercapto-benzimidazole	0.09 per cent by weight
Sodium mercaptobenzthiazole	0.01 per cent by weight
Ethyleneglycol	97.02 per cent by weight

For purposes of comparison the following known anti-freeze compounds were produced:

COMPARATIVE COMPOUND 1
(corresponding to DE—PS 11 54 976)

Borax	1.0 per cent by weight
Sodium nitrite	0.35 per cent by weight
Sodium nitrate	0.30 per cent by weight
Sodium benzoate	2.25 per cent by weight
Sodium metasilicate	0.03 per cent by weight
1,2,3-benztriazole	0.07 per cent by weight
Ethyleneglycol	96.00 per cent by weight

COMPARATIVE COMPOUND 2
(corresponding to DE—PS 14 92 522, Example 5)

Borax	3.50 per cent by weight
Benztriazole	0.10 per cent by weight
Sodium metasilicate-pentahydrate	0.10 per cent by weight
Picric acid	0.10 per cent by weight
Sodium nitrite	0.10 per cent by weight
Water	1.56 per cent by weight
Sodium hydroxide	0.62 per cent by weight
Ethyleneglycol	93.92 per cent by weight

Testing for corrosion protection was carried out by various test methods, viz:

1. ASTM D 1384—70 (1975) and also modifications of this method in regard to the test metals, anti-freeze compound concentration and temperature.
2. EMPA corrosion test and modifications of this method in regard to test metals and the anti-freeze agent concentrations.
3. FVV Guidelines for testing the suitability of coolant additives for coolant liquids for internal combustion engines.

The results of the comparative tests show that the anti-freeze compounds of the invention (Examples 1, 2 and 3) come off best overall, particularly at low concentrations of anti-freeze compound and also vis-a-vis special aluminium alloys (cf. Tables 1—6). From Table 7 the advantages which can be achieved with an addition of lead nitrate or sodium hexafluorosilicate according to the invention can be seen; Table 8 gives the corresponding results with anti-cavitation compounds.

TABLE 1: Corrosion test as per ASTM D 1384

Loss in weight in mg/cm² (+ = increase in weight through formation of protective coating)
Concentration: 33⅓ per cent by volume

	Copper	Solder	Brass	Steel	Cast Iron	Cast Aluminium
Example 1	0.05	0.03	0.05	+0.02	+0.05	+0.08
Example 2	0.05	0.06	0.05	+0.01	+0.06	+0.07
Example 3	0.02	0.04	0.02	+0.02	+0.04	+0.08
Comparative Compound 1	0.06	0.20	0.09	0.14	1.65	+0.02
Comparative Compound 2	0.00	0.03	0.00	0.03	0.03	0.08

TABLE 2: Corrosion test as per ASTM D 1384 with additional aluminium alloys.

Loss in weight in mg/cm² (+ = increase in weight as a result of formation of protective coating)
Concentration: 33⅓ per cent by volume.

	Copper	Solder	Brass	Steel	Cast Iron	Cast aluminium	$AlSi_{12}$	AlMn
Example 1	0.06	0.05	0.08	+0.01	+0.04	+0.07	+0.09	0.01
Example 2	0.05	0.11	0.05	+0.01	+0.07	+0.07	+0.07	+0.04
Example 3	0.02	0.04	0.02	+0.02	+0.04	+0.08	+0.04	+0.07
Comparative Compound 2	0.05	0.03	0.05	±0.00	0.05	0.10	0.04	0.23

TABLE 3: Corrosion test as per ASTM D 1384 at elevated temperature
(Boiling point of anti-freeze / water mixture: 104°C)

Concentration: 25 per cent by volume
Loss in weight in mg/cm² (+ = increase in weight by a formation of protective coating)

	Copper	Solder	Brass	Steel	Cast Iron	Cast Aluminium
Example 3	0.04	0.03	0.04	+0.01	0.02	0.05
Comparative compound 1	0.02	0.44	0.04	0.59	0.34	0.19

TABLE 4: Corrosion test as per EMPA

Losses in weight in mg/cm² (+ = increase in weight by formation of protective coating)
Concentration: 33⅓ per cent by volume.

	Soft solder on copper	Brass	Steel	Cast Iron	Aluminium cast alloy (Silafont)	Aluminium wrought alloy (Avional)
Example 3	0.10	0.03	+0.01	0.07	+0.11	+0.10
Comparative compound 1	0.3	0.03	0.07	0.05	0.05	0.02
Comparative compound 2	0.16	0.10	0.36	0.42	0.04	±0.00

TABLE 5: Modified corrosion test according to EMPA

(15 per cent by vol.anti-freeze; modified metal combination)
Loss in weight in mg/cm² (+ = increase in weight by formation of prptective coating)

	Copper	Soft solder on Copper	Brass	Steel	Cast iron	Aluminium cast alloy ($alSi_6Cu_3$)	Aluminium wrought alloy ($AlCuMg_2$)
Example 1	0.03	0.01	0.04	+0.01	0.09	0.05	+0.11
Example 3	0.04	0.0	0.04	+0.00	0.11	+0.09	+0.09
Comparative compound 1	0.02	0.07	0.03	0.09	7.18	1.68	1.40
Comparative compound 2	0.01	0.28	0.02	0.11	0.31	0.94	1.54

TABLE 6: Testing of anti-freeze by the FVV Guidelines, Vol. R 315

Corrosion inspections for ageing of coolant liquids
Concentration: 20 per cent by volume
Loss in weight in g/m² (+ = increase in weight by formation of protective coating)

	Copper	Soft solder	Brass	Steel	Grey cast iron	Aluminium alloys $AlCuMg_2$	$AlSi_{10}$ 10MgCu
Example 3	0.39	1.52	0.14	0.47	0.38	1.72	0.74
Comparative compound 1	0.64	1.81	0.17	0.95	16.75	7.61	7.99
Comparative compound 2	0.06	0.96	0.10	+0.46	+0.10	10.9	17.0

TABLE 7: Modified corrosion test according to EMPA

(50 per cent by vol. anti-freeze; modified metal combination)
Loss in weight in mg/cm² (+ = increase in weight by formation of protective coating)

	Steel (C 10)	Electrolytic copper and solder (Sn 40)	Brass (Ms 60)	Cast Iron (GG 25)	Zinc	$AlSi_6Cu_4$	$AlSi_{10}MgCu$	$AlSi_{12}$
Example 3 + 0.001% by weight lead nitrate	+0.01	0.10	+0.02	+0.06	+0.04	+0.34	0.04	0.08
Example 3 + 0.05% by weight sodium hexafluorosilicate	+0.10	+0.28	0.03	+0.13	+0.23	+0.03	+0.11	+0.12
Example 3	+0.03	0.53	+0.09	+0.09	+0.17	+0.21	+0.13	+0.10

TABLE 8: Testing of anti-freeze for cavitation according to the FVV Guidelines, Vol. R 315

All data are losses in weight.

		$Al\ Cu\ Mg_2$			Cast Iron	
	10% by vol. mg/hr	20% by vol. mg/hr	50% by vol. mg/hr	10% by vol. mg/hr	20% by vol. mg/hr	50% by vol. mg/hr
Example 3: no Cavitation protection	72.72	15.03	15.42	7.70	6.90	5.20
Example 1: with polymer additive After ageing	14.42	14.80 11.59	13.81	6.60	5.10	4.10
Example 1: with phosphoric ester	11.70	7.50	7.80	6.60	5.00	4.20

CLAIMS

1. Anti-freeze for coolant liquids, containing 1,2-alkyleneglycols, alkali salts of boric acid, alkali silicates, benztriazole, mercaptobenzimidazole, nitrophenols or their alkali salts which may be substituted with alkyl radicals, alkali nitrite, alkali nitrates, alkanolamines and alkali hydroxides, in which the alkali hydroxides are present in a quantity such that when the anti-freeze compound is diluted with water in the proportion of 1:1 to 1:3 there results a pH of 8.0 to 9.0, characterised by the following composition:

a) 1.0 to 4.0 per cent by weight of an alkali salt of boric acid,
b) 0.03 to 0.3 per cent by weight of alkali silicate,
c) 0.05 to 1.0 per cent by weight of alkali hydroxide,
d) 0.03 to 0.2 per cent by weight of benztriazole,
e) 0.03 to 0.3 per cent by weight of nitrophenols or their alkali salts, possibly substituted with methyl radicals,
f) 0.05 to 0.3 per cent by weight of alkali nitrite,
g) 0.05 to 0.4 per cent by weight of alkali nitrate,
h) 0.01 to 0.3 per cent by weight of alkanolamine,
i) 0.005 to 0.3 per cent by weight of ethoxylated mercaptobenzimidazole,
k) remainder: 1,2-alkyleneglycols and possibly small quantities of water as solubiliser.

2. An anti-freeze in accordance with Claim 1, characterised by the following composition:

a) 2.5 to 3.5 per cent by weight borax or
b) 1.3 to 1.8 per cent by weight disodium tetraborate,
c) 0.05 to 0.1 per cent by weight benztriazole,
d) 0.05 to 0.15 per cent by weight picric acid,
e) 0.10 to 0.20 per cent by weight sodium nitrate,
f) 0.20 to 0.30 per cent by weight potassium nitrate,
g) 0.05 to 0.15 per cent by weight sodium metasilicate pentahydrate,
h) 0.05 to 0.15 per cent by weight triethanolamine,
i) 0.01 to 0.2 per cent by weight of ethoxylated mercaptobenzimidazole,
k) 0.1 to 0.5 per cent by weight sodium hydroxide,
l) remainder: ethyleneglycol and/or 1,2-propyleneglycol and also possibly small quantities of water as solubilizer.

3. An anti-freeze in accordance with Claims 1 or 2, characterised by a content of 0.005 to 0.3 per cent by weight of mercaptobenzthiazole or its sodium salt.

4. An anti-freeze in accordance with any one of the Claims 1 to 3, characterised by a content of 0.001 to 0.3 per cent by weight of sodium hexafluorosilicate and/or lead nitrate.

5. An anti-freeze in accordance with any one of the Claims 1 to 4, characterised by the inclusion of anti-foam agents and/or anti-cavitation agents.

Printed for Her Majesty's Stationery Office by the Courier Press, Leamington Spa, 1981. Published by the Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained.